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DETERMINATION OF UNLIKE INTERACTIONS FROM BINARY VISCOSITY

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ABSTRACT.. Experimental viscosity data for the binary gaseous mixtures He–A, Ne–A and H_2–C_3H_8 have been utilised for determining the potential parameters for unlike pairs on the L–J (12 6) model. Three different methods have been employed, the first method being applicable only to mixtures exhibiting a maxima with respect to variations in the composition. The other two methods can be used for all gas pairs for which accurate viscosity data are available in a wide temperature range. The parameters thus obtained are tabulated along with those from other sources.

1. INTRODUCTION

Intermolecular potentials between like molecules have been determined with sufficient accuracy by the use of equilibrium and transport properties. For calculating transport properties of pure gases, the force constants used are those determined mainly from viscosity data. There is, however, considerable uncertainty in the values of the force parameters for unlike molecules as determined from the experimental data of inter-diffusion and thermal diffusion, the properties utilised by many workers. This is due to the non-availability of accurate data over a large temperature range and in the case of thermal diffusion there is the additional complication that the higher approximation terms are not negligible. So for the theoretical calculations of the transport properties of mixtures, the force constants for unlike pairs are calculated by the help of some semi-empirical combination rules which are not rigorously true. It is therefore important to be able to derive the unlike interaction parameters by other methods. Recently, Hirschfelder, Taylor and Kihara (1960) have pointed out that the accurate measurements of viscosity of gaseous mixtures as a function of both temperature and concentration can provide a good method of determining the unlike intermolecular forces.

In the present work three different methods have been developed for the determination of the unlike force parameters, provided accurate experimental data are available.

2. THEORY AND FORMULAE

On the basis of the Chapman-Enskog theory, the transport properties have been expressed in terms of a set of reduced collision integrals $\Omega^{(l,s)*}$ which depend

on the law of molecular interaction and are tabulated by Hirschfelder, Curtiss and Bird (1954) for different potential forms. The Lennard-Jones (12 : 6) potential is given by the relation

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where $\phi(r)$ is the potential energy between two molecules separated by a distance r, σ is the value of r at $\phi(r) = 0$ and ϵ is the depth of the potential well.

The viscosity of a binary gas mixture η_{mix}, to the first approximation, is given by

$$[\eta_{mix}]_1 = \frac{1+Z_\eta}{X_\eta + Y_\eta} \tag{2}$$

with

$$X_\eta = \frac{x_1^2}{\eta_1} + \frac{2x_1x_2}{\eta_{12}} + \frac{x_2^2}{\eta_2}$$

$$Y_\eta = \frac{3}{5} A_{12}^* \left\{\frac{x_1^2}{\eta_1}\left(\frac{M_1}{M_2}\right) + \frac{2x_1x_2}{\eta_{12}} \cdot \left(\frac{(M_1+M_2)^2}{4M_1M_2}\right) \cdot \left(\frac{(\eta_{12})^2}{\eta_1\eta_2}\right) + \frac{x_2^2}{\eta_2}\left(\frac{M_2}{M_1}\right)\right\}$$

$$Z_\eta = \frac{3}{5} A_{12}^* \left\{ x_1^2 \cdot \left(\frac{M_1}{M_2}\right) + 2x_1x_2\left[\left(\frac{(M_1+M_2)^2}{4M_1M_2}\right)\left(\frac{\eta_{12}}{\eta_1} + \frac{\eta_{12}}{\eta_2}\right) - 1\right] + x^2{}_2 \left(\frac{M_2}{M_1}\right)\right\}$$

x_1, x_2 are the mole fractions, η_1, η_2 the viscosities and M_1, M_2 are the molecular weights of components 1 and 2 respectively. η_{12} is the viscosity of a hypothetical gas given by

$$\eta_{12} \times 10^7 = 266{\cdot}93 \cdot \frac{\sqrt{2M_1M_2T/(M_1+M_2)}}{\sigma_{12}^2 \Omega_{12}^{(2,2)*}(T_{12}^*)} \tag{3}$$

3. DETERMINATION OF THE POTENTIAL PARAMETERS

(a) Hirschfelder, *et al.* (1960) have obtained the relation for the maximum or minimum of the viscosity of binary gas mixtures, by differentiating Eq. (2) with respect to x_1 and equating $(d\eta_{mix}/dx_1)$ to zero. The relation for the maximum or minimum viscosity may be written in the form

$$\frac{(\eta_{mix})_{max}}{(\eta_1\eta_2)^{1/2}} = \frac{\beta_c(\beta+\beta^{-1}) - 2\beta_c}{\beta_c^2 - 1}$$

where $$\beta = (\eta_1/\eta_2)^{1/2} \quad \ldots (4)$$

and $$\beta_c = K(2R)^{-1}(1-\alpha+f) \quad \ldots (5)$$

with $$R = (M_1+M_2)^{1/2}/(4M_1M_2)^{1/4}$$

$$K = \frac{\sigma_1\sigma_2\sqrt{\Omega_{11}^{(2,2)*}(T^*).\Omega_{22}^{(2,2)*}(T^*)}}{\sigma_{12}^2\Omega_{12}^{(2,2)*}(T_{12}^*)} \quad \ldots (6)$$

$$\alpha = 3/5\ A_{12}^* \text{ and } f^2 = (1-\alpha)^2+4\alpha R^4$$

Here for getting maximum in the viscosity β must lie between β_c and β_c^{-1}.

The maximum value of experimental viscosity is obtained from the graph of η_{mix} against x_1 for each temperature. This is substituted in Eq. (4) along with the experimental values of η_1 and η_2 and the equation solved for β_c. Let the values of β_c at two temperatures T_1, T_2 be $(\beta_c)_1$, $(\beta_c)_2$. Then using the subscripts 1 and 2 to denote the quantities at temperatures T_1 and T_2 we get from eqns. (5) and (6)

$$(\beta_c)_1/(\beta_c)_2 = \frac{K_1}{K_2} \cdot \frac{(1-\alpha_1+f_1)}{(1-\alpha_2+f_2)} \quad (7)$$

and $$K_1/K_2 = \left(\frac{\Omega_{12}^{(2,2)*}(T_2^*)}{\Omega_{12}^{(2,2)*}(T_1^*)}\right) \cdot \left(\frac{\Omega_{11}^{(2,2)*}(T_1^*)}{\Omega_{11}^{(2,2)*}(T_2^*)} \frac{\Omega_{22}^{(2,2)*}(T_1^*)}{\Omega_{22}^{(2,2)*}(T_2^*)}\right) \quad (8)$$

With the help of the Eqns. (7) and (8) and the tabulations of Hirschfelder *et al.* (1954), for the collision integrals and A_{12}^*, the ratio $(\beta_c)_1/(\beta_c)_2$ is calculated for a number of arbitrarily chosen values of ϵ_{12}/k and a graph drawn for $(\beta_c)_1/(\beta_c)_2$ versus ϵ_{12}/k. The desired value of ϵ_{12}/k for the gas pair is then read from the graph corresponding to the value of $(\beta_c)_1/(\beta_c)_2$ determined from Eq. (4). The value of σ_{12} can be calculated easily with the help of Eqns. (5) and (6) by using this value of ϵ_{12}/k.

In the present work the force parameters for He–A and H_2–C_3H_8 interaction have been calculated by this method. For He–A, the recent data of Rietveld, *et al.* (1953) at temperatures 291·1°K, 229·5°K and 192·5°K could be successfully combined to give three sets of ϵ_{12}/k and σ_{12} values, the mean of which is recorded in Table I. Only one set of force constants of H_2–C_3H_8 could be obtained as the data at only two temperatures 500°K and 550°K taken from Trautz and Kurz (1931) could be used successfully.

This method can give accurate and consistent values for force constants, provided accurate experimental data are available even at two temperatures but it is applicable to only those binary gas mixtures which show maxima or minima in viscosity at some concentration.

(b) *Method of Intersection* :

The graphical methods of intersection and Lennard-Jones translation discussed in detail by Srivastava and Srivastava (1959) can be successfully used for obtaining the unlike force parameters on the L-J (12 : 6) potential from the data on viscosity of gas mixtures. For this purpose Eq. (2) is solved for η_{12} giving

$$\eta_{12} = \frac{-b \pm \sqrt{b^2-4ac}}{2a} \qquad \ldots (9)$$

where $a = \frac{6}{5} A_{12}^* \cdot \left(\frac{x_1 x_2}{\eta_1 \eta_2} \right) \left(\frac{(M_1+M_2)^2}{4M_1M_2} \right) \cdot (\eta_{mix} - \eta_1 - \eta_2)$

$$b = \frac{3}{5} A_{12}^* \left[2x_1x_2 + x_1^2 \cdot \left(\frac{M_1}{M_2} \right) \cdot \left(\frac{\eta_{mix}}{\eta_1} \right) + x_2^2 \cdot \left(\frac{M_2}{M_1} \right) \left(\frac{\eta_{mix}}{\eta_2} \right) - x_1^2 \cdot \left(\frac{M_1}{M_2} \right) - x_2^2 \left(\frac{M_2}{M_1} \right) \right] + \eta_{mix} \left(\frac{x_1^2}{\eta_1} + \frac{x_2^2}{\eta_2} \right) - 1$$

and

$$c = 2x_1x_2\eta_{mix}$$

Now by substituting the experimental values of η_1, η_2 and η_{mix} at any temperature, η_{12} is obtained in terms of A^*_{12} which is a temperature dependent function and whose values are tabulated by Hirschfelder, *et al.* (1954). Then η_{12} is calculated for one temperature by substituting the value of A^*_{12} corresponding to any arbitrarily chosen value of ϵ_{12}/k and by using this η_{12} value the corresponding σ_{12} value can be obtained from Eq. (3). In this way a set of ϵ_{12}/k and σ_{12} values are calculated at one temperature. The same process is repeated for getting sets of values of ϵ_{12}/k and σ_{12} at other temperatures. Graphs are then plotted for ϵ_{12}/k against σ_{12} at each temperature. The intersection point gives the required values of ϵ_{12}/k and σ_{12} for the gas pair.

This method has been utilised to determine the force parameters for the gas pairs He–A and Ne–A. There is usually some uncertainty in exactly locating the intersection point when the experimental data are not very accurate. In view of the extensive data on mixture viscosities, however, this method can serve as a useful supplement to other methods for determining unlike force parameters.

(c) *Translation Method* :

If experimental data are available in a large range of temperature, the translation method can be applied with the following device. From table, A^*_{12} is found to vary very slowly with T^* and can therefore be taken to be constant over a very small range of T^*, say, for a change of about 3%. It is thus possible

to calculate A^*_{12} at any temperature with sufficient accuracy by using the value of ϵ_{12}/k obtained from the combination rule, as the true value of ϵ_{12}/k is not likely to differ from the combination rule values by more than about 3%. Knowing A^*_{12} in this manner, η_{12} can be determined from Eq. (9) by utilising the experimental values of η_{mix}, η_1 and η_2. Thus knowing η_{12} at different temperatures and using Eq. (3), the Lennard-Jones translation method can be applied for getting ϵ_{12}/k and σ_{12}. In case this value of ϵ_{12}/k is much different from the value previously selected from the combination rule, the process can be repeated by using this refined value of ϵ_{12}/k.

This method is used here for determining the force parameters for the gas pairs He–A and Ne–A.

4. RESULTS

The force parameters determined by these methods are given in Table I along with those determined from other sources.

TABLE I

Unlike Force Parameters on the L–J (12 : 6) model

Gas Pair	Force Parameters	Present work			Previous work			Ref. for data
		From maximum viscosity	Intersection method	Translation method	Comb. rules	From inter-diffusion	From Thermal diffusion	
He–A	ϵ_{12}/k°K	36.97	36.97	36.9	35.6	33.8[a]	37.91[b]	A
	σ_{12}Å	2.96	2.985	3.028	2.997	2.99	3.025	
Ne–A	ϵ_{12}/k°K	..	69.0	66.37	66.6	64.5[c]	67.6[b]	B
	σ_{12}Å	..	2.943	2.932	3.104	3.098	3.079	
H_2–C_3H_8	ϵ_{12}/k°K	103.8	..	..	98.25	..	..	C
	σ_{12}Å	4.019	..	..	3.988	..	..	

(A) Rietveld and Itterbeek (1953).
(B) Trautz and Binkele (1930).
(C) Trautz and Kurz (1931)
(*a*) Srivastava and Srivastava (1959)
(*b*) Saxena (1955)
(*c*) Srivastava (1959).

5. DISCUSSION

It will be seen from the table that the three methods employed here give quite consistent values of the unlike force parameters which agree well with the values obtained from the combination rules. This shows clearly that the viscosity data on mixtures of gases can be employed to give quite reliable values for the unlike interaction parameters. Unfortunately the large amount of exist-

ing data on mixture viscosities had never been directly utilised so far for calculating the unlike force parameters. The present investigations show that this is quite feasible and desirable.

The values of the unlike parameters obtained by others using thermal diffusion data show good agreement with the present determinations, but those obtained from inter-diffusion data exhibit noticeable discrepancies. It is worth nothing that in the evaluation of the unlike force parameters from inter-diffusion data, the force parameters for like interactions were not utilised, while all the other methods cited here depend upon the accuracy of the force parameters for pure components also.

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